

APPLICATION FOR UNITED STATES LETTERS PATENT

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INVENTION:

A GLAZING PANEL HAVING
SOLAR SCREENING PROPERTIES

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CROSS-REFERENCE TO RELATED APPLICATION

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~~This Application is a Composite Continuation of U.S. Application Number~~
08/660,755 filed June 10, 1996 and U.S. Application No. 08/660,756 filed June 10,
1996. This Application claims the priority of United Kingdom Patent Application No.
5 95 11 691.9 filed June 9, 1995 and United Kingdom Patent Application No. 95 14 190.9
filed July 12, 1995, and titled "A glazing panel having solar screening properties and a
process for making such a panel.", the subject matter of which is incorporated herein by
reference.

BACKGROUND OF THE INVENTION

1. Field of the invention

The present invention relates to a glazing panel having solar screening properties.
The panel according to one aspect of the invention takes the form of a substrate carrying
a spray-formed pyrolytic coating containing tin and antimony. According to another
15 aspect of the invention the invention takes the form of a substrate carrying a coating
containing tin and antimony formed by chemical vapor deposition.

Reflective transparent solar control glazing panels have become a useful material
for architects to use for the exterior facade of buildings. Such panels have aesthetic
qualities in reflecting the immediate environment and, being available in a number of
20 colors, in providing a design opportunity. Such panels also have technical advantages by

providing the occupants of a building with protection against solar radiation by reflection and/or absorption and eliminating the dazzling effects of intense sunshine, giving an effective screen against glare, enhancing visual comfort and reducing eye fatigue.

From a technical point of view, it is desired that the glazing panel shall not pass too great a proportion of total incident solar radiation in order that the interior of the building shall not become overheated in sunny weather. The transmission of total incident solar radiation may be expressed in terms of the "solar factor". As used herein, the term "solar factor" means the sum of the total energy directly transmitted and the energy which is absorbed and re-radiated on the side away from the energy source, as a proportion of the total radiant energy incident of the coated glass.

Reflective transparent solar control glazing has also become much used in vehicle windows, where the objective is to protect the vehicle occupants against solar radiation. It has been used in railway carriages as side windows and in road vehicles for side, rear and roof windows. It has further been proposed to form the whole roof area of a motor car. It serves to provide protection against solar radiation by reflection and/or absorption and by eliminating the dazzling effects of intense sunshine, thereby giving an effective screen against glare, enhancing visual comfort and reducing eye fatigue. In this case the main energy factor to be considered is the total energy directly transmitted (TE), since the energy which is internally absorbed and re-radiated (AE) is dissipated by the

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movement of the vehicle. The essential aim of the vehicle panel is thus to have a low TE factor.

The properties of the coated substrate discussed herein are based on the standard definitions of the International Commission on Illumination - *Commission Internationale de l'Eclairage* ("CIE").

The standard illuminants quoted herein are CIE Illuminant C and Illuminant A. Illuminant C (mostly used for evaluating the optical properties of glazing panels for buildings) represents average daylight having a color temperature of 6700°K. Illuminant A (which equates to the light emitted by car headlamps and is therefore generally used to evaluate the optical properties of glazing panels for motor vehicles) represents the radiation of a Planck radiator at a temperature of about 2856°K.

The "luminous transmittance" (TL) is the luminous flux transmitted through a substrate as a percentage of the incident luminous flux.

The "luminous reflectance" (RL) is the luminous flux reflected from a substrate as a percentage of the incident luminous flux.

The "energy transmission" (TE) is the total radiant energy directly transmitted through a substrate as a percentage of the incident radiant energy.

The "energy reflection" (RE) is the radiant energy reflected from a substrate as a percentage of the incident radiant energy.

The "solar factor" (FS) is the ratio of the sum of the total energy directly transmitted through a substrate (TE) and the energy which is absorbed and re-radiated on the side away from the energy source (AE) as a proportion of the total radiant energy incident on the substrate.

The "selectivity" of the coated substrate relates to the balance between luminous transmission and energy transmission. In the case of building glass it is often defined as the ratio of the luminous transmittance to the solar factor (TL/FS), but for vehicle glass it commonly refers to the ratio of the luminous transmittance to the energy transmission (TL/TE).

The "dominant wavelength" (lD) is the peak wavelength in the range transmitted or reflected by the coated substrate.

The "purity" (p) of the color of the substrate refers to the excitation purity measured with Illuminant C. It is specified according to a linear scale on which a defined white light source has a purity of zero and the pure color has a purity of 100%. The purity of the coated substrate is measured from the side opposite the coated side.

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The "emissivity" (e) is the ratio of the energy emitted by a given surface at a given temperature to that of a perfect emitter (black body with emissivity of 1.0) at the same temperature.

The term "refractive index" (n) is defined in the CIE International Lighting

5 Vocabulary, 1987, page 138.

2. Description of the Related Art

A number of techniques are known for forming coatings on a vitreous substrate, including pyrolysis. Pyrolysis generally has the advantage of producing a hard coating, which precludes the need for a protective layer. The coatings formed by pyrolysis have durable abrasive- and corrosion-resistant properties. It is believed that this is due in particular to the fact the process involves depositing of coating material onto a substrate which is hot. Pyrolysis is also generally cheaper than alternative coating processes such as sputtering, particularly in terms of the investment in plant. The deposit of coatings by other processes, for example by sputtering, led to products with very different properties, in particular a lower resistance to abrasion and occasionally a different refractive index.

A wide variety of coating materials have been proposed for glazing panels, and for several different desired properties of the glazing. Tin oxide, SnO_2 , has been widely used, often in combination with other materials such as other metal oxides. GB Patent 1455148 teaches a method for pyrolytically forming a coating of one or more oxides on

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a substrate, primarily by spraying compounds of a metal or silicon, so as to modify the light transmission and/or light reflection of the substrate, or to impart antistatic or electrically conductive properties. Its examples of specified oxides include ZrO_2 , SnO_2 , Sb_2O_3 , TiO_2 , Co_3O_4 , Cr_2O_3 , SiO_2 and mixtures thereof. Tin oxide (SnO_2) is seen as advantageous because of its hardness and its ability to have antistatic or electrically conductive properties. GB Patent 2078213 relates to a sequential spray method for pyrolytically forming a coating on a vitreous support and is particularly concerned with tin oxide or indium oxide as the main coating constituents. When its metal coating precursor is tin chloride this is advantageously doped with a precursor selected from ammonium bifluoride and antimony chloride in order to increase the electrical conductivity of the coating.

It is also known that where a coating of tin oxide is formed by pyrolysis of SnCl_4 , the presence of a dopant such as antimony chloride SbCl_5 , directly mixed with the tin chloride SnCl_4 , improves the absorption and reflection of some near solar infrared radiation.

Our earlier Patent, GB 2200139, describes and claims a method of forming a pyrolytic tin oxide coating on a hot glass substrate by spraying a solution containing a tin compound and additives which produce in the coating both fluorine and such materials as antimony, arsenic, vanadium, cobalt, zinc, cadmium, tungsten, tellurium and manganese so as to give the coating a low emissivity and a low specific internal haze factor. While

the resultant coating has many desirable properties it falls short of the combination of properties now being sought.

SUMMARY OF THE INVENTION

5 It is an object of the present invention to provide a pyrolytically formed glazing panel having solar screening properties.

We have discovered that this and other useful objectives can be achieved by utilising chemical vapor deposition (CVD) to apply a pyrolytic coating comprising tin and antimony oxides in a specific relative ratio.

10 Thus, according to a first aspect of the present invention, there is provided a glazing panel comprising a vitreous substrate carrying a tin/antimony oxide coating layer containing tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.14, the said coating layer having been pyrolytically formed by chemical vapor deposition, whereby the so-coated substrate has a solar factor FS of less than 70%.

15 It is a further object of the present invention to provide a glazing panel having a high level of solar screening properties in combination with other desirable properties of luminous transmission and high selectivity.

We have discovered that this and other useful objectives can be achieved by a vitreous substrate bearing a thick pyrolytically sprayed coating comprising tin and
20 antimony oxides in a specific relative ratio.

Thus, according to a second aspect of the present invention, there is provided a glazing panel comprising a vitreous substrate carrying a spray-formed pyrolytic tin/antimony oxide coating layer having a thickness of at least 400 nm and containing tin and antimony in a Sb/Sn molar ratio of from 0.05 to 0.14, whereby the coated substrate has a luminous transmittance (TL) of less than 35% and a selectivity (TL/TE) of at least 1.3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments relating the the first aspect of the invention will initially be described.

The substrate is preferably in the form of a ribbon of vitreous material, such as glass or some other transparent rigid material. In view of the proportion of incident solar radiation which is absorbed by the glazing panel, especially in environments where the panel is exposed to strong or long-term solar radiation, there is a heating effect on the glass panel which may require that the glass substrate be subsequently subjected to a toughening process. However, the durability of the coating enables the glazing panel to be mounted with the coated face outermost, thus reducing the heating effect.

Preferably, the substrate is clear glass, although this aspect of the invention also extends to the use of colored glass as the substrate.

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The Sb/Sn molar ratio in the coating layer is preferably at least 0.03, most preferably at least 0.05. This assists in ensuring a high level of absorption. On the other hand the said ratio is preferably less than 0.21, with a view to achieving a high level of luminous transmittance (TL). Most preferably the ratio is less than 0.15, since above this level the coating layer displays an unduly high level of absorption, coupled with poor selectivity.

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Coated substrates according to the invention offer the advantage of a luminous reflectance (RL) of less than 11%. This low level of reflection in a building glazing panel is much favoured by architects. It avoids the panels creating glare in the vicinity of the building.

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It may be useful to prevent interaction between the glass of the substrate and the tin/antimony oxide coating layer. As an example, it has been found that in the pyrolytic formation of a tin oxide coating from tin chloride on a soda-lime glass substrate, sodium chloride tends to become incorporated into the coating as a result of reaction of the glass with the coating precursor material or its reaction products, and this leads to haze in the coating.

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Thus, an intermediate haze-reducing coating layer is preferably positioned between the substrate and the tin/antimony oxide coating layer. The haze-reducing layer may be pyrolytically formed in an incompletely oxidized state by contacting the substrate in an undercoating chamber with undercoat precursor material in the presence of oxygen

in insufficient quantity for full oxidation of the undercoat material on the substrate. The expression "incompletely oxidized material" is used herein to denote a true sub-oxide, that it to say an oxide of a lower valency state of a multivalent element (for example VO_2 or TiO), and also to denote an oxide material which contains oxygen gaps in its

5 structure: an example of the latter material is SiO_x where x is less than 2, which may have the general structure of SiO_2 but has a proportion of gaps which would be filled with oxygen in the dioxide.

We prefer the haze-reducing coating layer to comprise a silicon oxide having a geometric thickness such as about 100 nm. The presence of a silicon oxide undercoating on soda-lime glass has the particular benefit of inhibiting the migration of sodium ions from the glass whether by diffusion or otherwise into the tin/antimony oxide coating layer either during formation of that upper layer or during a subsequent high temperature treatment.

10 Alternatively, the undercoat may be constituted as an "anti-reflection" undercoating such as, for example, an oxidized aluminum/vanadium layer as described in GB Patent specification 2248243.

15 The glazing panels according to the invention have a solar factor of less than 70%, preferably less than 60% and in some instances preferably less than 50%. The preference for a solar factor of less than 60% arises when the panels according to the invention are positioned with the coated side facing the exterior, i.e. facing the energy

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source. Generally, this positioning leads to a improved solar factor compared with the positioning of the panel with the coated side away from the energy source. The need for a solar factor of less than 50% arises for buildings in parts of the world with high levels of solar energy. For vehicle sunroofs an even lower solar factor may be desirable.

5 The use of colored glass is one way of providing a lower solar factor, and is commonly employed in both building glass and vehicle glass. In comparing the effectiveness of coating layers it is therefore necessary to take into account any differences between the types of glass on which the respective coatings are deposited. Thus one example of a coating according to the invention on clear glass gave a solar factor of 63 %, whereas an equivalent coating on a green colored glass gave a solar factor of 44.5%.

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15 It is also desired that the glazing panel shall also transmit a reasonable proportion of visible light in order to allow natural illumination of the interior of the building or vehicle and in order to allow its occupants to see out. Thus it is desirable to increase the selectivity of the coating, that is to increase the ratio of the transmittance to the solar factor. Indeed it is preferred that the selectivity be as high as possible.

20 In general it is preferred that the luminous transmittance (TL) of the panel according to the invention is between 40 and 65 %. Nevertheless, a panel having a light transmittance below 40% may be used as a roofing panel, for example as a vehicle sunroof.

Preferably, the tin/antimony oxide coating has a thickness of from 100 to 500 nm. Thick layers of tin/antimony oxide, particularly layers having a low Sb/Sn molar ratio, can provide a glazing panel with the advantageous combination of a low solar factor (FS) and low emissivity. Another way of obtaining this combination is to deposit
5 on the tin/antimony oxide layer of the invention a low-emissivity layer of doped tin oxide, for example tin oxide doped with fluorine. However this is disadvantageous in the sense that it makes necessary the deposition of a supplementary layer, which is time-consuming and expensive.

In principle, another way to provide a combination of low solar factor and low
10 emissivity could be to form a tin/antimony oxide layer containing a doping agent such as fluorine. For example, GB Patent 2200139 teaches a method of forming a pyrolytic tin oxide coating by spraying a solution which in addition to the tin precursor contains compounds which will result in the coating containing fluorine and at least one of antimony, arsenic, vanadium, cobalt, zinc, cadmium, tungsten, tellurium and
15 manganese.

Thus one could, for instance, form a coating from reactants containing tin, antimony and fluorine in the ratios $Sb/Sn = 0.028$, $F/Sn = 0.04$. However we have discovered that the presence of fluorine has the apparent disadvantage of hindering the incorporation of antimony in the coating rather than effectively reducing the emissivity.

20 For example reactants containing antimony and tin in the ratio $Sb/Sn = 0.028$ gave a

coating with an Sb/Sn ratio of about 0.057, whilst the same reactants plus a fluorine-containing reactant in an amount such that $F/Sn = 0.04$ gave a coating with an Sb/Sn ratio of about 0.038.

The invention accordingly presents the advantage of simultaneously providing a solar factor (FS) below 60%, an emissivity of less than 0.4 (preferably less than 0.3) and a luminous transmittance (TL) of more than 60%. Thus the coated product fulfil two important functions. In winter it maintains the heat in the building, because of its low emissivity. In summer it resists the passage of solar heat into the building and thus avoids overheating inside the building, thanks to its low solar factor. This is especially achieved for coatings having an Sb/Sn ratio between 0.01 and 0.12, especially 0.03 to 0.07, and a thickness between 100 and 500 nm, for example between 250 and 450 nm.

Preferably the tin/antimony oxide coating layer is an exposed coating layer and the glazed panel comprises only one such tin/antimony oxide coating layer.

However, it is possible to provide one or more further coating layers, whether by pyrolysis or by other coating methods, to achieve certain desired optical qualities. It should be noted however, that the tin/antimony oxide layer when applied by pyrolysis has sufficient mechanical durability and chemical resistance to suitably serve as the exposed layer.

The panels according to the invention may be installed in single or multi-glazed assemblies. While the coated surface of the panel may be the inside surface of the

exterior glazing panel so that the coated surface is not exposed to the ambient weather conditions which might otherwise more rapidly reduce its life by soiling, physical damage and/or oxidation, coatings produced by pyrolysis generally have a greater mechanical resistance than coatings produced by other methods and they may therefore
5 be exposed to the atmosphere. The panels according to the invention may usefully be employed in laminated glass structures, for example where the coated surface is the inside surface of the exterior laminate.

When it is desired to manufacture pyrolytically coated flat glass, it is best to do so when the glass is newly formed. To do so has economic benefits in that there is no
10 need to reheat the glass for the pyrolytic reactions to take place, and it also has benefits as to the quality of the coating, since it is assured that the surface of the glass is in pristine condition. Preferably, therefore, said coating precursor material is brought into contact with an upper face of a hot glass substrate constituted by freshly-formed flat glass.

15 Thus, the glazing panels according to the invention may be manufactured as follows. Each pyrolytic coating step may be carried out at a temperature of at least 400°C, ideally from 550°C to 750°C. The coatings can be formed on a sheet of glass which moves in a tunnel oven or on a glass ribbon during formation, whilst it is still hot. The coatings can be formed inside the lehr which follows the glass ribbon forming

device or inside the float tank on the top face of the glass ribbon whilst the latter is floating on a bath of molten tin.

The coating layers are applied to the substrate by chemical vapor deposition (CVD). This is a particularly beneficial method because it provides for coatings of regular thickness and composition, such uniformity of the coating being particularly important where the product is to cover a large area. CVD offers many advantages over pyrolysis methods using sprayed liquids as the reactant materials. With such spray methods it is difficult both to control the vaporization process and to obtain a good uniformity of coating thickness. Moreover, the pyrolysis of sprayed liquids is essentially limited to the manufacture of oxide coatings, such as SnO_2 and TiO_2 . It is also difficult to make multi-layer coatings using sprayed liquids because every coating deposition produces a significant cooling of the substrate. Furthermore, chemical vapor deposition is more economic in terms of raw materials, leading to lower wastage.

The product with a CVD coating is physically different from those with coatings obtained by spraying. Notably a spray coating retains traces of the sprayed droplets and of the path of the spray gun, which is not the case with CVD.

To form each coating, the substrate is brought into contact, in a coating chamber, with a gaseous medium comprising the reactant mixture in the gaseous phase. The coating chamber is fed with the reactant gas through one or more nozzles, the length of which is at least equal to the width to be coated.

Methods and devices for forming such a coating are described for example in French Patent No. 2 348 166 (BFG Glassgroup) or in French Patent application No. 2 648 453 A1 (Glaverbel). These methods and devices lead to the formation of particularly strong coatings with advantageous optical properties.

5 To form the coatings of tin/antimony oxide, two successive nozzles are used. The reactant mixture comprising the sources of tin and antimony are fed in at the first nozzle. Where this mixture comprises chlorides which are liquid at ambient temperature, it is vaporized in a current of anhydrous carrier gas at an elevated temperature. Vaporization is facilitated by the atomization of these reagents in the carrier gas. To produce the oxides, the chlorides are brought into the presence of water vapor
10 conducted to the second nozzle. The water vapor is superheated and is also injected into a carrier gas.

Advantageously, nitrogen is used as the substantially inert carrier gas. Nitrogen is sufficiently inert for the purposes in view, and it is inexpensive when compared with
15 the noble gases.

Undercoatings of silicon oxide SiO_2 or SiO_x may be deposited from silane SiH_4 and oxygen in accordance with the descriptions in British Patent specifications GB 2234264 and GB 2247691.

If a glass substrate bearing an incompletely oxidized coating is exposed to an
20 oxidizing atmosphere for a sufficiently long period of time, it may be expected that the

coating will tend to become fully oxidized so that its desired properties are lost.

Therefore, such undercoat is over-coated with the tin/antimony oxide coating layer while it is still in an incompletely oxidized state, and while the substrate is still hot, thereby to preserve such undercoat in an incompletely oxidized state. The time during which the freshly undercoated glass substrate may be exposed to an oxidizing atmosphere such as air and before the undercoat is over-coated, without damaging the properties of the undercoat, will depend on the temperature of the glass during such exposure and on the nature of the undercoat.

Advantageously, said undercoating chamber is surrounded by a reducing atmosphere. The adoption of this feature assists in preventing ambient oxygen from entering the undercoating chamber and accordingly allows better control of the oxidizing conditions within that undercoating chamber.

The oxygen required for the undercoating reactions may be supplied as pure oxygen, but this adds unnecessarily to costs, and it is accordingly preferred that air is supplied to the undercoating chamber in order to introduce oxygen thereto.

It will be noted that the Sb/Sn molar ratio which is desirable in the reactant mixture does not always correspond to that ratio which is desirable for the tin/antimony coating layer

Preferably the source of tin is selected from SnCl_4 , monobutyl trichloro tin ("MBTC") and mixtures thereof. The source of antimony may be selected from SbCl_3 ,

SbCl₃, organo antimony compounds and mixtures thereof. Examples of suitable source materials are Sb(OCH₂CH₃)₃, Cl_{1.7}Sb(OCH₂CH₃)_{1.3}, Cl₂SbOCHClCH₃, Cl₂SbOCH₂CHCH₃Cl and Cl₂SbOCH₂C(CH₃)₂Cl.

This aspect of the invention will now be described in more detail, with reference to the following non-limiting examples.

In the Examples the Sb/Sn molar ratio in the coating layers was determined by an X-ray analysis technique in which the number of X-ray counts of the respective elements was compared. While this technique is not as precise as if a calibration by chemical dosage were made, the similarity of antimony and tin means that they respond similarly to X-rays. The ratio of the measured number of observed counts of the respective elements thus provides a close approximation to their molar ratio.

Colored rather than clear glass was employed as indicated in some of the Examples. The properties of the respective types of colored glass are shown in Table 1.1 below. In all cases the properties were measured on glass samples having a thickness of 4 mm, this being the thickness of glass employed in all the examples except Examples 1.1 to 1.7 (for which the thicknesses are shown in Table 1.2). The initials in the headings to this and the other following tables (TL, TE etc.) have the meanings described above.

With regard to the calculation of the solar factor, it should be noted that for luminous transmittances (TL) below 60% the effect of low emissivity is not negligible

and should be taken into account: as the emissivity reduces so equally does the solar factor.

Table 1.1

Glass Type	Green A	Green B	Grey	Medium Grey	Dark Grey
λD in transmission (nm) [Illuminant: C/A]	505.4/508.5	504.9/508.4	470.1/493.9	493.2/502.7	478.9/502.7
Purity (%)	2.9/3.4	2.1/2.5	1.5/0.8	5.6/5.1	2.6/1.8
TL (%) [Illuminant: C/A]	72.66/71.12	78.44/77.20	55.65/55.56	36.80/35.76	22.41/22.30
TE (%) (CIE)	44.0	52.3	56.9	25.9	31.11
FS (%) coated side (CIE)	56.8	62.9	66.3	43.4	47.3
TL/FS [Illuminant: C]	1.28	1.25	0.84	0.85	0.47

EXAMPLE 1.1

Clear soda-lime float glass advancing at a speed of 7 meters per minute along a float chamber was undercoated at a coating station located at a position along the float chamber where the glass was at a temperature of about 700°C. The supply line was fed with nitrogen, silane was introduced thereto with a partial pressure of 0.25%, and oxygen was introduced with a partial pressure of 0.5% (ratio 0.5). A coating of silicon oxide SiO₂ having a thickness of 100nm was obtained.

The undercoated substrate, having a thickness of 6 mm was then immediately coated by CVD pyrolysis using a coating apparatus comprising two successive nozzles.

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A reagent comprising a mixture of SnCl_4 as a source of tin and SbCl_5 as a source of antimony was used. The Sb/Sn molar ratio in the mixture was about 0.2. The reactant mixture was vaporised in a current of anhydrous nitrogen gas at about 600°C , was fed in at the first nozzle. Vaporization was facilitated by the atomization of these reagents in the carrier gas. Superheated water vapor was conducted to the second nozzle. The water vapor was heated to about 600°C , and was also injected into a carrier gas, which was air heated to about 600°C . The flow rate of gas (carrier gas + reagent) in each nozzle was 1 m³/cm width of substrate per hour, at the operating temperature.

The coating process was continued until the geometrical thickness of the tin/antimony oxide coating superimposed on the undercoated substrate was 185 nm.

EXAMPLES 1.2 TO 1.7

In Examples 1.2 to 1.7, the procedure of Example 1.1 was followed but with variations in such parameters as the reactant mixture, the presence or absence of an undercoat oxide, the ratio of Sb/Sn in the coating and in the reactant mixture and the thickness of the glass substrate. For instance, compared with Example 1.1, in Example 1.2 no undercoating was applied and the tin/antimony oxide coating layer had a thickness of 210 nm. The reactant mixtures were as follows:

Examples 1.2 and 1.3: the same as in Example 1.1 (but with a lower concentration of the reactant mixture in the carrier gas in Example 1.3);

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chamber where the glass was at a temperature of about 700°C. The supply line was fed with nitrogen, silane was introduced thereto with a partial pressure of 0.2%, and oxygen was introduced with a partial pressure of 0.5% (ratio 0.55). A coating of silicon oxide SiO_x, with x approximately equal to 1.8, was obtained with a refractive index of about 1.7. The thickness of the coating was 40 nm.

The undercoated substrate, having a thickness of 4 mm, was then coated by CVD pyrolysis. A reagent comprising a mixture of MBTC as a source of tin and Cl_{11.7}Sb(OCH₂CH₃)_{1.3} as a source of antimony was used. The Sb/Sn molar ratio in the mixture was about 0.195 (mass ratio 0.2). The reactant mixture was vaporized in a current of anhydrous air at about 200°C, fed in at the nozzle. Vaporization was facilitated by the atomization of these reagents in the carrier gas. Superheated water vapor was then introduced, heated to about 200°C.

The coating process was continued until the geometrical thickness of the tin/antimony oxide coating superimposed on the undercoated substrate was 120 nm.

EXAMPLES 1.9 TO 1.14

In Examples 1.9 to 1.14, the procedure of Example 1.8 was followed but with variations as shown in the accompanying Table 1.2 in such parameters as the thickness of the undercoat, the ratio of Sb/Sn in the coating and in the reaction mixture, the

thickness of the tin/antimony oxide coating layer and the color of the glass. The results of examples 1.8 to 1.14 are set out in Table 1.3.

The glazing panels according to the Examples 1.9 to 1.14 had a pleasant blue color in transmission, the dominant wavelength in transmission in the visible wavelength lying within the range of 470 to 490 nm (Illuminant C).

In a variant of Example 1.9 in which the Green A glass was replaced by Medium Grey glass, the resultant luminous transmittance (TL) was 20%, the luminous reflectance (RL) was 10% and the energy transmission (TE) was 15 %.

EXAMPLES 1.15 TO 1.30

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~~The procedure of Example 1.1 was followed for further Examples 1.15 to 1.30 with variations in the reactant mixture, the color and thickness of the glass substrate, the thickness of undercoat oxide, and the ratio of Sb/Sn in the reactant mixture and in the coating. For Examples 1.15 to 1.22 the reactant mixture was MBTC and $\text{Cl}_{11.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$ without trifluoroacetic acid whereas for Examples 1.23 to 1.30 the reactant mixture was MBTC and $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$ with trifluoroacetic acid. The E/Sn ratio in the reactant mixture for these examples was 0.04.~~

The variations in operating parameters, and the results obtained, are set out in the accompanying Table 1.4 for Examples 1.15 to 1.22 and in the accompanying Table 1.5

for Examples 1.23 to 1.30. The silicon oxide SiO_x used in Examples 1.15 to 1.30 had a value of x approximately equal to 1.8.

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Table 1.2

Example	1.1	1.2	1.3	1.4	1.5	1.6	1.7
Tin/antimony oxide thickness (nm)	185	210	105	120	105	445	110
Undercoat oxide	SiO ₂	absent	absent	SiO ₂	SiO ₂	SiO ₂	SiO ₂
Undercoat thickness (nm)	100	0	0	70	70	70	70
Sb/Sn ratio in coating	0.48	0.48	0.46	0.19	0.15	0.06	0.18
Sb/Sn ratio in reactants	0.20	0.20	0.20	0.20	0.20	0.10	0.20
Haze (%)	0.07	2.09	4.36 to 7.01	low	low	low	low
TL (%)	45.7	44.3	65.5	51.0	61.6	47.5	55.0
RL (%) (coated side)	9.0	12.0	18.8	12.0	11.7	6.6	13.7
FS (%) (coated side) (CIE)	55.3	56.9	66.0	58.4	62.2	47.2	59.6
TL/FS	0.83	0.78	0.99	0.87	0.99	1.01	0.92
λ_D in transmission (nm)	587.5	-560	480.1	478.8	481.0	483.0	479.3
Colour purity in transmission (%)	3.4	3.9	4.9	11.5	8.7	8.0	10.3
λ_D in reflection from the coated side (nm)	472.3	494.5	575.3	579.5	577.6	490.0	577.0
Colour purity (%) in reflection from the coated side	36.9	7.0	19.1	35.0	35.2	6.0	33.1
Emissivity	>0.7	>0.7	>0.7	0.84	0.71	0.25	0.79
Glass thickness (mm)	6	6	6	5	5	5	5

Table 1.3

Example	1.8	1.9	1.10	1.11	1.12	1.13	1.14
Tin/antimony oxide thickness (nm)	120	120	320	470	470	320	470
Undercoat oxide	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂	SiO ₂
Undercoat thickness (nm)	40	70	40	40	40	40	40
Sb/Sn ratio in coating	0.10	0.18	0.09	0.09	0.09	0.09	0.09
Sb/Sn ratio in reactants	0.07	0.20	0.07	0.07	0.07	0.07	0.07
Haze (%)	0.36	0.1	1.0	1.8	1.8	1.0	1.8
TL (%) [Illuminant A/Illuminant C]	53/55	39/20	31/32	31/32	9/9	40/41	36 [A]
RL (%) (coated side) [Illuminant A/C]	9/10	11/11	7/7	7/7	7/7	8/7	7 [A]
RL (%) (uncoated side) [Illuminant C]	8	8	6	6	5	7	-
TE (%) (CIE)	31	25	25	18	9	21	27
FS (%) (coated side) (CIE)	45	41	41	36	29	39	43
TL/FS	1.2/1.2	0.95/0.98	0.76/0.78	0.86/0.89	0.31/0.31	1.02/1.05	5.4 [A]
λ_D in transmission (nm)	505.5/498.6	497.2/487.0	494.8/481.9	497.2/487.2	494.2/480.0	501.0/491.6	493.4 [A]
Colour purity in transmission (%)	4.4/4.2	6.2/8.9	4.9/8.1	7.6/10.8	7.0/11.8	7.2/8.6	5.4 [A]
λ_D in reflection from the coated side (nm)	487.9/478.1	-572.5/566.9	-511.8/512.2	-576.9/559.8	-555.4/550.1	-512.5/513.6	-576.0 [A]
Colour purity (%) in reflection from the coated side	7.4/14.6	2.2/2.9	17.2/16.3	6.0/1.2	2.1/6.6	15.4/14.5	1.5 [A]
Emissivity	0.71	0.85	0.44	0.35	0.35	0.44	0.35
Colour of glass	Green A	Green A	Grey	Green B	Dark grey	Green A	Clear soda lime

Table 1.4

Example	1.15	1.16	1.17	1.18	1.19	1.20	1.21	1.22
Tin/antimony oxide thickness (nm)	320	320	320	320	390	390	390	390
Undercoat oxide	SiO _x	SiO _x	SiO _x	SiO _x	SiO _x	SiO _x	SiO _x	SiO _x
Undercoat thickness (nm)	60 (approx)	60 (approx)	60 (approx)	60 (approx)	80 (approx)	80 (approx)	80 (approx)	80 (approx)
Sb/Sn ratio in coating	0.053	0.053	0.053	0.053	0.058	0.058	0.058	0.058
Sb/Sn ratio in reactants	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028
Haze (%)	0.65	0.65	0.65	0.65	1.2	1.2	1.2	1.2
TL (%) [Illuminant C]	68.8	55.7	60.1	28.2	61.0	49.2	25.0	53.1
RL (%) (coated side)	8.9	8.2	8.4	7.2	9.0	8.0	7.2	6.9
RL (%) (uncoated side)	8.9	7.3	7.8	5.0	7.8	6.5	4.8	8.2
TE (%) (CIE)	50.8	28.3	33.1	15.8	43.0	24.5	13.7	28.5
FS (%) (coated side) (CIE)	60.3	43.6	47.2	34.4	54.7	40.9	32.9	40.1
TL/TE	1.35	2.00	1.82	1.75	1.42	1.96	1.79	1.86
TL/FS	1.15	1.27	1.28	0.82	1.11	1.20	0.76	1.20
λ_D in transmission (nm)	524.0	506.2	506.0	494.0	496.0	500.7	493.4	499.5
Colour purity in transmission (%)	0.5	3.1	2.3	5.8	2.2	4.7	7.5	4.1
λ_D in reflection from the coated side (nm)	482.9	484.2	484.0	482.9	-495.2	-493.8	-495.0	-550.3
Colour purity (%) in reflection from the coated side	14.5	16.2	15.8	18.0	5.0	4.4	6.4	7.0
Emissivity	0.29	0.29	0.29	0.29	0.27	0.27	0.27	0.27
Colour of glass	Clear	Green A	Green B	Med. grey	Clear	Green A	Med. grey	Green B

Table 1.5

Example	1.23	1.24	1.25	1.26	1.27	1.28	1.29	1.30
Tin/antimony oxide thickness (nm)	290	290	290	290	410	410	410	410
Undercoat oxide	SiO _x	SiO _x	SiO _x	SiO _x	SiO _x	SiO _x	SiO _x	SiO _x
Undercoat thickness (nm)	80 (approx)	80 (approx)	80 (approx)	80 (approx)	90 (approx)	90 (approx)	90 (approx)	90 (approx)
Sb/Sn ratio in coating	0.038	0.038	0.038	0.038	0.037	0.037	0.037	0.037
Sb/Sn ratio in reactants	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028
Haze (%)	0.82	0.82	0.82	0.82	1.2	1.2	1.2	1.2
TL (%) [Illuminant C]	70.2	56.7	61.0	28.7	64.2	51.9	26.9	56.4
RL (%) (coated side)	10.0	9.0	9.2	8.0	8.8	8.1	7.2	8.3
RL (%) (uncoated side)	9.5	8.0	8.3	5.2	7.7	6.6	4.8	6.9
TE (%) (CIE)	54.3	29.5	34.7	16.6	47.2	26.1	14.6	30.6
FS (%) (coated side) (CIE)	63.0	44.5	48.3	34.9	57.7	42.0	33.6	45.4
TL/TE	1.30	1.90	1.74	1.71	1.36	2.00	1.73	1.81
TL/FS	1.11	1.27	1.27	0.83	1.10	1.24	0.76	1.24
λ_D in transmission (nm)	581.3	538.8	549.4	498.5	568.6	535.9	502.7	543.7
Colour purity in transmission (%)	2.9	2.9	2.7	3.3	3.5	3.7	3.6	3.5
λ_D in reflection from the coated side (nm)	510.3	508.6	508.9	507.2	549.3	505.1	491.8	507.0
Colour purity (%) in reflection from the coated side	8.1	10.1	9.6	11.3	3.3	1.1	1.2	1.0
Emissivity	0.28	0.28	0.28	0.28	0.23	0.23	0.23	0.23
Colour of glass	Clear	Green A	Green B	Med. grey	Clear	Green A	Med. grey	Green B

Preferred embodiments relating the the second aspect of the invention will now be described.

The substrate is preferably in the form of a ribbon or sheet of vitreous material, such as glass or some other transparent rigid material. In view of the proportion of incident solar radiation which is absorbed by the glazing panel, especially in environments where the panel is exposed to strong or long-term solar radiation, there is a heating effect on the panel which may require that the substrate be subsequently subjected to a toughening process. However, the durability of the coating enables the panel to be mounted with the coated face outermost, thus reducing the heating effect.

Preferably the substrate is formed of colored glass. It is found that the combination of coloration within the material of the glass and a coating according to the invention facilitates the achievement of the required low luminous transmission and high selectivity. The generally preferred colors for glass used in vehicle roofs, side or rear windows are grey and green.

The tin/antimony oxide coating preferably has a thickness of from 400 to 800 nm, most preferably 450 to 700 nm. Such thicknesses permit the achievement of a low total transmitted energy factor (TE) while retaining a sufficient level of light transmission. Thick layers of tin/antimony oxide, particularly layers having a low Sb/Sn molar ratio, can not only provide a glazing panel with the required low luminous

transmission and high selectivity but also with the advantageous combination of a low solar factor FS and low emissivity.

It may be useful to prevent interaction between the glass of the substrate and the tin/antimony oxide coating layer. As an example, it has been found that in the pyrolytic formation of a tin oxide coating from tin chloride on a soda-lime glass substrate, sodium chloride tends to become incorporated into the coating as a result of reaction of the glass with the coating precursor material or its reaction products, and this leads to haze in the coating. Thus, an intermediate haze-reducing coating layer may if desired be positioned between the substrate and the tin/antimony oxide coating layer. Such an intermediate layer is generally unnecessary for low luminous transmission panels since the haze is not noticeable to any significant extent. If used it may comprise a silicon oxide having a geometric thickness such as about 100nm. The presence of a silicon oxide undercoating on soda-lime glass has the benefit of inhibiting the migration of sodium ions from the glass whether by diffusion or otherwise into the tin/antimony oxide coating layer either during formation of that upper layer or during a subsequent high temperature treatment.

Panels according to this aspect of the invention are particularly well suited to use as vehicle roof panels, for example to tilting or sliding sunroofs, or even to form substantially the whole of the vehicle roof area. They may also advantageously be used as vehicle rear or rear side windows.

Glazing with a luminous transmittance of less than 35 % is advantageous as a vehicle roof panel, most particularly if the panel is to form most or all of the roof area. While such a low level of luminous transmission is required according to the invention, it is also desirable that the glazing panel shall transmit some visible light in order to give
5 a contribution to the natural illumination of the interior of the vehicle.

A high level of selectivity of the coating in combination with a low level of luminous transmission allows a low solar energy transmission. The selectivity provided by this aspect of the invention is essentially at least 1.3 and preferably at least 1.5. It is a particular benefit of this aspect of the invention that in practice it permits the
10 achievement of selectivity values close to 2.

The energy transmission (TE) is therefore preferably less than 15%, most preferably less than 10%. Such low energy transmission assists in reducing the load on a vehicle air conditioning system.

For a whole-roof panel it may be advantageous to employ a panel with a
15 luminous transmittance as low as 10% and energy transmission of just 5%, giving a selectivity of 2. For an opening roof panel somewhat higher transmission is generally preferred, for example luminous transmittance of about 20% and energy transmission of about 12 %, again giving a selectivity approaching 2.

The Sb/Sn molar ratio in the coating is preferably in the range 0.07 to 0.20, most
20 preferably 0.08 to 0.15. The preferred ranges arise from the need to have sufficient

antimony to be effective in giving the required low transmission properties while not being present in sufficient amounts to affect the optical quality.

Conveniently the coating comprises simply a single layer of tin/antimony oxide. However, it is possible to provide one or more further coating layers, whether applied by pyrolysis or by other coating methods, to achieve certain desired optical qualities. It should be noted however, that the tin/antimony oxide layer when applied by pyrolysis has sufficient mechanical durability and chemical resistance to suitably serve as the exposed layer. Alternatively the said layer can be applied to the surface of the substrate that is to face the interior of a vehicle.

The panels according to the invention have properties of low reflectivity of visible light which are particularly advantageous for vehicle glazing. Preferably the reflectivity of visible light (RL) is lower than 12%, and may typically be between 5 and 12%.

The panels according to the invention may be installed in single or multi-glazed assemblies. The coating layers are applied to the hot substrate by spraying reactants in a liquid state, for example by means of a spray nozzle. While liquid spraying lacks the precision of alternative pyrolytic method of chemical vapor deposition (CVD), it is a convenient and inexpensive method for deposition of a thick coating layer, as in the present case. Indeed CVD is generally not a convenient method for the formation of thick coatings.

Especially in the preferred instance of applying the coating to a colored substrate any variations, resulting from the use of a spray method, in thickness or uniformity of the coating are barely visible. Preferably the source of tin is SnCl_2 and the source of antimony is SbCl_3 , both materials being added to water for the spraying operation.

5 Dissolved organometallic material may also be used.

When it is desired to manufacture pyrolytically coated flat glass, it is best to do so when the glass is newly formed. To do so has economic benefits in that there is no need to reheat the glass for the pyrolytic reactions to take place, and it also has benefits as to the quality of the coating, since it is assured that the surface of the glass is in
10 pristine condition. Preferably, therefore, said coating precursor material is brought into contact with an upper face of a hot glass substrate constituted by freshly-formed flat glass.

Thus, the glazing panels according to the invention may be manufactured as follows. The pyrolytic coating step may be carried out at a temperature of at least
15 400°C, ideally from 550°C to 750°C.

To form each coating, the substrate is brought into contact, in a coating chamber, with a spray of droplets containing the antimony- and tin-containing reactants. The spray is applied by one or more spray nozzles arranged to follow a path which provides the coating across the width of the ribbon to be coated.

In a spray-pyrolysis method the Sb/Sn molar ratio in the finished coating is not directly proportional to the ratio in the reactant mixture, and indeed is usually substantially different therefrom. The level of incorporation of antimony into the coating is significantly affected by such parameters as the spray rate, the type of glass and the glass temperature. Attempts to compute the coating proportions from the starting proportions are therefore unreliable and it is usually necessary to undertake preliminary trials to determine the starting proportions to meet the required coating proportions in a specific instance.

Following deposition the coatings are preferably polished, using any desired conventional polishing means. The coated product may also if desired be subjected to tempering.

This aspect of the invention will now be described in more detail with reference to the following non-limiting examples.

In the Examples the Sb/Sn molar ratio in the coating layers was determined by an X-ray analysis technique in which the number of X-ray counts of the respective elements was compared. While this technique is not as precise as if a calibration by chemical dosage were made, the similarity of antimony and tin means that they respond similarly to X-rays. The ratio of the measured number of observed counts of the respective elements thus provides a close approximation to their molar ratio.

EXAMPLES 2.1 TO 2.21

In all the examples a Sb/Sn mixture was applied in an aqueous mixture to a moving ribbon of hot glass substrate having a thickness of 4 mm. Several different types of glass were employed, as shown in Table 2A below. The initials in the headings to this and the other following tables (TL, TE etc.) have the meanings described above. The columns FS p1 and FS p2 in Table 2C refer to the solar factor at, respectively, the side of the glass facing the light source (position1) and the side remote from the light source (position2). Unless otherwise indicated the properties shown in the tables were measured under illuminant C. Under the conditions described the difference in TL between using illuminant C and illuminant A (more generally used in the field of automobile vehicles) was minimal, being of the same order of magnitude as routine errors of measurement.

In each case the mixture was a coating precursor solution containing approximately 1000g (in total) of SnCl_2 and SbCl_3 per litre of the mixture and in the proportions shown in Table 2B below. The solution was applied to the substrate by a reciprocating spray nozzle which followed a path across the width of the ribbon.

Table 2A

Glass Type	Clear	Green A	Green C	Grey	Med. Grey 1	Med. Grey 2
λ D in transmission (nm) [Illuminant: C/A]		505.4/508.5	509.7/510.2	470.1/493.9	493.2/502.7	494.6/502.8
Purity (%)		2.9/3.4	3.2/4.0	1.5/0.8	5.6/5.1	9.9/9.3
TL (%) [Illuminant: C/A]	89.0	72.66/71.12	67.36/65.69	55.65/55.56	36.8/35.8	37.07/35.13
TE (%) (CIE)	83.0	44.0	37.1	56.9	25.9	20.9
TL/TE (CIE C)	1.07	1.65	1.81	0.98	1.42	1.77
FS p1 (CIE) (%)	86.0	56.8	51.7	66.3	43.4	39.7
TL/FS	1.03	1.28	1.30	0.84	0.85	0.93

The sprayed tin and antimony components reacted to form a pyrolytic tin oxide coating on the glass. The parameters employed and the results obtained are shown in Tables 2B and 2C.

It will be noted that Examples 2.4 and 2.5 do not satisfy the requirements of the claims herein in respect of the required coating thickness and selectivity and in the case of Example 2.5 also in respect of the required luminous transmission. These examples are included for comparison to show how operating outside the scope of the claims produces inferior results.

Table 2B

Example	Glass Type	Sb/Sn of reactants	Sb/Sn of coating	Coating thickness (nm)	TL (%)	RL (%)
2.1	Clear	0.20	0.11	535	23.0	10.0
2.2	Clear	0.20	0.12	470	27.0	10.0
2.3	Clear	0.30	0.14	670	13.0	10.0
2.4	Clear	0.30	0.16	306	27.0	11.0
2.5	Clear	0.30	0.19	119	56.0	10.0
2.6	Green A	0.30	0.17	670	10.4	9.9
2.7	Green C	0.30	0.14	670	9.6	9.9
2.8	Med. Grey 2	0.30	0.14	520	6.4	10.5
2.9	Med. Grey 2	0.30	0.14	520	6.5	10.5
2.10	Green A	0.20	0.11	530	15.7	10.3
2.11	Green C	0.20	0.11	530	17.3	10.3
2.12	Med. Grey 1	0.20	0.11	530	9.5	10.2
2.13	Med. Grey 2	0.20	0.11	530	9.6	10.2
2.14	Grey	0.175	0.11	640	15.0	10.0
2.15	Grey	0.175	0.11	530	19.0	10.0
2.16	Green A	0.175	0.11	640	19.0	10.0
2.17	Green A	0.175	0.11	530	25.0	10.0
2.18	Green C	0.175	0.11	640	17.8	10.0
2.19	Green C	0.175	0.11	530	23.0	10.0
2.20	Med. Grey 1	0.175	0.11	640	10.0	10.0
2.21	Med. Grey 2	0.175	0.11	530	12.6	10.0

Table 2C

Example	TE (%)	RE (%)	FS p1 (%)	FS p2 (%)	Emissivity (n)	TL/TE	TL/FS
2.1	17.0	11.0	35.0	31.0	0.35	1.35	0.66
2.2	21.0	11.0	38.0	39.0		1.29	0.71
2.3	10.0	11.0	30.0	26.0		1.30	0.43
2.4	25.0	13.0	41.0	42.0	0.53	1.08	0.66
2.5	51.0	13.0	60.0	61.0	0.76	1.14	0.97
2.6	5.8	10.9	26.8	22.9	0.35	1.80	0.39
2.7	5.1	10.9	26.3	22.3	0.35	1.90	0.36
2.8	4.2	10.9	25.6	22.0	0.40	1.52	0.25
2.9	3.5	10.9	25.1	21.5	0.40	1.86	0.26
2.10	10.0	11.1	29.9	25.8	0.35	1.87	0.62
2.11	8.7	11.1	28.9	24.8	0.35	1.99	0.60
2.12	5.5	11.0	26.6	22.3	0.35	1.73	0.36
2.13	4.8	11.0	26.0	21.7	0.35	2.00	0.37
2.14	10.0	11.0	30.0			1.50	0.50
2.15	14.0	11.0	33.0			1.36	0.58
2.16	9.8	11.0	29.8			1.94	0.64
2.17	13.0	11.0	32.0			1.92	0.78
2.18	8.6	11.0	28.9			2.07	0.62
2.19	11.0	11.0	31.0			2.09	0.74
2.20	5.4	11.0	26.5			1.85	0.38
2.21	7.7	11.0	27.7			1.77	0.45

As variations to Examples 2.14 and 2.20, coatings were obtained having a thickness of 730 nm and an Sb/Sn ratio of 0.10. In both cases the resulting properties were substantially the same as the original Examples 2.14 and 2.20.

The product coated substrate in all the examples had a blue tint in transmission,

- 5 with a dominant wavelength (D) between 470 and 490 nm, and a haze value between 0.7 and 1.1.

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